



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
26.05.2021 Bulletin 2021/21

(51) Int Cl.:
C23C 18/24 ^(2006.01) **C25B 1/24** ^(2021.01)
C25B 1/28 ^(2021.01) **C25B 9/08** ^(2006.01)
C25B 11/04 ^(2021.01) **C25B 11/16** ^(2006.01)

(21) Application number: **19210726.6**

(22) Date of filing: **21.11.2019**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME KH MA MD TN

(72) Inventors:
• **TESSER Giorgio**
31046 Oderzo (IT)
• **DALBIN Sandrine**
31052 Maserada Sul Piave (IT)

(71) Applicant: **COVENTYA S.p.A.**
22060 Carugo (CO) (IT)

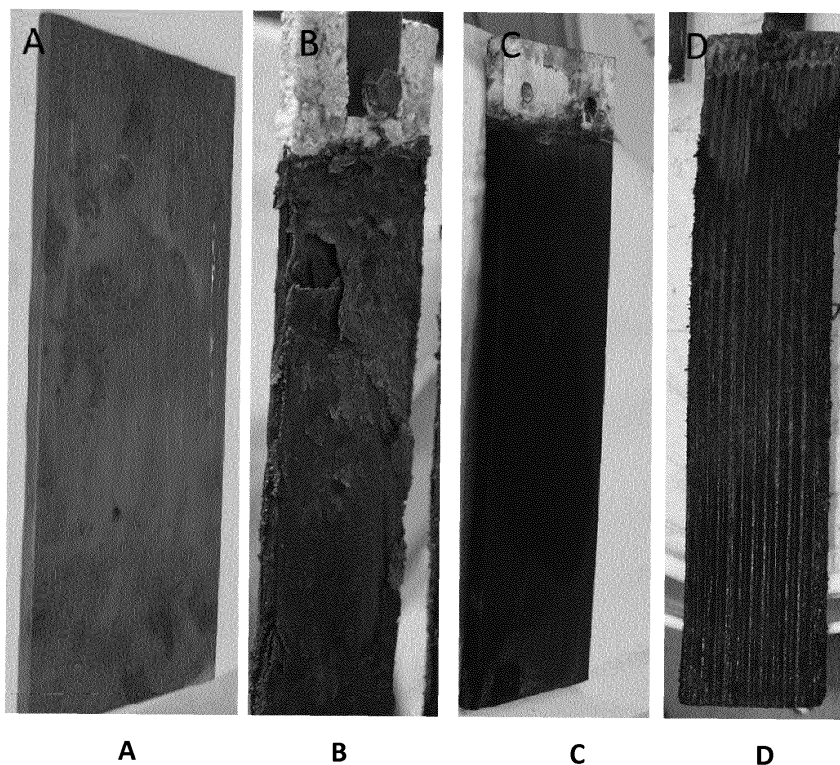
(74) Representative: **Pfenning, Meinig & Partner mbB**
Patent- und Rechtsanwälte
Theresienhöhe 11a
80339 München (DE)

(54) **AN ELECTROLYTIC TREATMENT DEVICE FOR PREPARING PLASTIC PARTS TO BE METALLIZED AND A METHOD FOR ETCHING PLASTIC PARTS**

(57) The present invention refers to an electrolytic treatment device having an anodic compartment comprising a non-chromium(VI) etching solution to be treated and immersed therein an anode. The anodic compartment is separated by a membrane from a cathodic compartment comprising a cathodic solution comprising an

inorganic acid, wherein the anode and the cathode are used comprising or consisting of a ternary or higher Pb alloy with Sn and at least one further metal selected from the group consisting of Sb, Ag, Co, Bi and combinations thereof. Moreover, a method for etching plastic parts is provided as well.

Fig. 1



Description

[0001] The present invention refers to an electrolytic treatment device having an anodic compartment comprising a non-chromium(VI) etching solution to be treated and immersed therein an anode. The anodic compartment is separated by a membrane from a cathodic compartment comprising a cathodic solution comprising an inorganic acid, wherein the anode and the cathode are used comprising or consisting of a ternary or higher Pb alloy with Sn and at least one further metal selected from the group consisting of Sb, Ag, Co, Bi and combinations thereof. Moreover, a method for etching plastic parts is provided as well.

[0002] For metallization of plastic parts, a pre-treatment step is necessary to create sufficient roughness and anchoring points at the surface of the plastic part. This pre-treatment is called etching. Subsequently, the metallization by sensitization of the surface and electroless deposition can be conducted.

[0003] For many years, the etching solution was based on a mixture of chromic acid and sulfuric acid. Out of safety reasons it is now better to avoid the use of toxic compounds like hexavalent chrome and chromic acid. Due to the REACH regulation, chromic acid has to be avoided. Out of these reasons new etching solutions have been developed which are free of hexavalent chromium.

[0004] One of the most efficient chromium VI free etching solutions is a mixture of permanganate with inorganic acid. However, the main problem of permanganate is its limited long-term stability, in particular at high temperatures and at an acidic pH.

[0005] Hence, there is a need to add a co-oxidant like periodate to the etching solution in order to re-oxidize the lower valence manganese products. However, after a certain period, all the periodate is reduced to iodate. To counter this effect, an electrolytic treatment of the solution is necessary to recover the periodate concentration and re-oxidize the iodate to periodate. This can be performed internally in the etching bath or parallel in a separated re-oxidation module. The oxidation of iodate to periodate will take place at the anode which is immersed in the etching solution. The cathode is separated from the etching solution by a membrane to prevent reduction of the etching solution.

[0006] Lead alloy anodes/cathodes are currently the preferred choice for this application as they are conductive, economical and relatively stable in solutions having a high oxidant concentrations and a low pH. The main drawback of this type of anodes/cathodes is the formation of a precipitate on their surface which restricts the performance of the oxidation process and renders necessary the cleaning of the anode/cathode.

[0007] JP 5403535 describes a method of electrolytically treating an etching solution containing a manganese salt as an active ingredient. The method refers to treating an etching solution electrolytically by using an electrolytic treatment apparatus having a cathode chamber separated from an etching solution to be treated by a cation exchange membrane made of a perfluorosulfonic acid resin and anodically oxidizing an etching solution having an increased concentration of a halogenate.

[0008] JP 2006225693 describes a method of electrolytically oxidizing an aqueous solution containing iodine and/or iodic acid by an electrolytic process to produce periodates, more specifically, in the electrolytic process, an insoluble iodate or the like insoluble on the anode surface.

[0009] Clancy, M., C. J. Bettles, A. Stuart, et N. Birbilis. 2013. « The influence of alloying elements on the electrochemistry of lead anodes for electrowinning of metals: A review ». Hydrometallurgy 131-132 (janvier): 144-57 describes the alloying elements used in lead alloy anodes and their effects on the electrochemistry and metallic properties of those alloys.

[0010] When starting from this prior art it was therefore the objective of the present invention to provide an electrolytic treatment device having an anode that is efficient for the re-oxidation process and shows low dissolution in the etching solution. Moreover, the process should be easy to handle and cost-effective. The process is applied at industrial level, lead anodes are heavy obviously for their density, so their maintenance (cleaning, substitution...) must be limited in frequency.

[0011] This problem is solved by the specific lead alloy employed in the electrolytic treatment device with the features of claim 1 and the method for etching plastic parts with the features of claim 8. The further dependent claims describe preferred embodiments.

[0012] According to the present invention an electrolytic treatment device is provided which comprises

- an anodic compartment comprising a non-chromium(VI) etching solution as anolyte and immersed therein an anode,
- a cathodic compartment comprising a cathodic solution comprising an inorganic acid as catholyte and immersed therein a cathode, and
- a membrane separating the anodic from the cathodic compartment.

The anode and/or the cathode of the device comprises a ternary or higher Pb alloy (e.g. a quaternary Pb alloy) with Sn

and at least one further metal selected from the group consisting of Sb, Ag, Co, Bi, and combinations thereof.

[0013] It was surprisingly found that the use of a ternary or higher lead alloy with Pb, Sn and at least one further metal, allows the generation of a stable PbO_2 catalytic layer on the surface of the anode in an acidic etching environment with a better performance compared to known binary lead alloys. The performance of the PbO_2 catalytic layer (formed on the anodic surface) is monitored by the capacity to oxidize the iodate in function of both the energy given to the re-oxidation module and the time. This is defined as the re-oxidation module rate, measured in g of iodate reoxidized by Ah applied. The stability of the ternary or higher alloy is also evaluated by measurement of its dissolution (the weight loss of the anode) in function of the immersion time in the high oxidant and acidic medium.

[0014] In a specific embodiment, the third metal is Sb. In a specific embodiment, the third metal is Co. In a specific embodiment, the third metal is Ag. In a specific embodiment, the third metal is Bi. Moreover, in case of a quaternary alloy, a specific embodiment comprises the third metal is Sb and the fourth metal is Ag, Bi or Co.

[0015] In a preferred embodiment, the alloy comprises from 85 to 95% Pb, preferably from 87 to 93% Pb, more preferably from 89 to 92% Pb.

[0016] In a preferred embodiment, the alloy comprises from 0,5 to 10% Sn, preferably from 1 to 8% Sn, more preferably from 1,5 to 7% Sn.

[0017] In a further preferred embodiment, the alloy is a ternary alloy and comprises from 0,05 to 10% of the third metal, preferably from 0,5 to 8% of the third metal, more preferably from 1 to 7% of the third metal.

[0018] A further preferred embodiment of the inventive etching solution comprises

- 47-74 wt% of at least one inorganic acid,
- 2,2-3,8wt% of at least one metaperiodate salts, preferably sodium metaperiodate,
- 0,01-0,06 wt% of at least one manganese salt,
- 0,01-0,64wt% of at least one iodate salt, preferably sodium iodate and
- water up to 100%.

In a preferred embodiment, the inorganic acid of the anolyte and/or the catholyte is phosphoric acid or sulfuric acid, preferably phosphoric acid.

[0019] Moreover, according to the present invention, a method for etching plastic is provided with the following steps:

- a) providing the electrolytic treatment device of any of the claims 1 to 6,
- b) immersing a plastic part in the etching solution as anolyte in the anodic compartment chamber, and
- c) applying a current from 1 to 8 A/dm² for re-oxidising the iodate to periodate in the anodic compartment.

[0020] It is preferred that during step c) the iodate in the etching solution is reoxidised to periodate.

[0021] In a preferred embodiment, the cathodic solution comprises a phosphoric acid. The anolyte (i.e. the etching solution) preferably comprises 54-74 wt%(weight percentage) phosphoric acid, 0-0,64 wt% Na iodate, 2-4 wt% Na metaperiodate, 0,01-0,06 wt% manganese salts, and water up to 100 wt%.

[0022] In a preferred embodiment, the temperature during the etching step is comprised from 50 to 80°C, more preferably from 60 to 70°C.

[0023] In a preferred embodiment, the re-oxidation rate of the module to re-oxidize the iodate to metaperiodate following this method is from 0,1 to 1 g/Ah, preferably from 0,2 to 0,8 g/Ah, more preferably from 0,3 to 0,6 g/Ah.

[0024] The re-oxidation rate refers to iodate oxidation and is measured at a specific flow of anolyte circulation between the etching tank and the anodic module compartment. It is measured from the concentration of iodate and periodate present in the etching bath before applying the current and the second measurement after different Ah applied to the module. Those concentrations can be measured by titration or by high-performance liquid chromatography (HPLC).

[0025] It represents the capacity to re-oxidize the iodate according the given energy to the electrolytic cell. A part of this energy serves to oxidize the iodate and the other to produce oxygen. The ideal solution would be that all of the energy was used to oxidize the iodate, but depending on the anode performance, more or less oxygen will be developed at the anode surface.

[0026] The dissolution of the anode immersed in the etching solution without any current applied is preferably from 0,1 to 3 g/dm² day, more preferably from 0,1 to 2 g/dm² day, and even more preferably from 0,1 to 1 g/dm² day.

[0027] It is preferred that the dissolution of the anode immersed in the etching solution (applied current from 0,8 to 1A/dm²) is from 0,05 to 0,8 g/dm² day, more preferably from 0,05 to 0,7 g/dm² day, and even more preferably from 0,05 to 0,6 g/dm² day.

[0028] The dissolution of the anode is measured by the weight loss of the anode over the immersion time in the etching solution.

[0029] With reference to the following figures and examples, the subject-matter according to the present invention is intended to be explained in more detail without wishing to restrict said subject-matter to the specific embodiments shown here.

[0030] Fig.1 shows different anodes after different exposition into re-oxidation conditions and with different operating conditions:

- A) Pb91 Sb2 Sn7 anode as raw material, before use
- B) Pb91 Sb2 Sn7 anode after immersion in etching anolyte applying 3A/dm² for 10 hours during workday and 0A/dm² for 14hours during pause at night
- C) Pb91 Sb2 Sn7 anode after immersion in etching anolyte applying 3A/dm² for 10 hours during workday and 1A/dm² for 14hours during pause at night
- D) Pb90 Sn10 anode after immersion with 3A/dm² during workday and 0A/dm² during pause at night

[0031] Fig.2 shows a HPLC chromatogram used for the measurement of the concentration of iodate and periodate. The retention peak for iodate can be observed on the chromatogram at 2,5 minutes and the retention peak for periodate at 5,1 minutes.

Examples

Preparation of the etching bath

[0032] The etching bath is prepared with the compounds found in the following table 1.

Table 1

Compounds	Concentration	Concentration range
KMnO ₄	0,03wt%	0,01 - 0,06wt%
NaIO ₄	3,20wt%	2,2 - 3,8wt%
Phosphoric acid 85%	67wt%	54,0 - 74,0wt%
NaIO ₃	0,6wt%	0 - 0,64wt%
H ₂ O	Up to 100wt%	Up to 100wt%

[0033] The bath temperature should be maintained around 60 to 70 °C.

Use of the anode

[0034] The anodes and cathodes are immersed respectively in the anodic and cathodic compartment and connected to the rectifier. The electrolytic treatment device is powered on at 3A/dm² and the anolyte is circulating from the etching tank to the anodic compartment at 4L/min flow. Different compositions of anodes were used during those tests and they are listed in table 2 below. Some of the anodes are presented on Fig 1.

Table 2

Anode composition	Reoxidation rate	Dissolution	Anode surface cleaning
Pb (99,9)	Continuous 0,2 g/Ah over Ah applied	0,9 g/dm ² day High dissolution rate Thin black powder and problem of bath filtration	Not necessary
Pb/Sn (90/10)	From 0,6 to 0 g/Ah in 60Ah	0,04 g/dm ² day	Cleaning every 60Ah
Pb/Ca/Sn (98,5/0,05/1,4)	From 0,6 to 0 g/Ah in 6h	0,04 g/dm ² day	Cleaning every 60Ah
Pb/Sb (95/5)	Continuous 0,5 g/Ah over Ah applied	0,88 g/dm ² day High dissolution	Not necessary

(continued)

Anode composition	Reoxidation rate	Dissolution	Anode surface cleaning
Pb/Sn/Sb (91/7/2)	Continuous 0,5 g/Ah over Ah applied	0,22 g/dm ² day	Not necessary
Pb/Sn/Ag (91/7/2)	From 0,5 to 0g/Ah in 3000Ah	0,20 g/dm ² day	Cleaning every 3000Ah

[0035] The anode dissolution is measured by the weight loss of the anode over the course of the experiment.

[0036] The re-oxidation rate has been measured by HPLC using a Symmetry C18 4.6x250mm 5 μ m (Waters) column and a detection at 220 nm. The result of such measurement are presented on Fig 2.

[0037] The results of our test show that we have obtained the best result with the Pb/Sn/Sb anode. They have a good re-oxidation rate with a low dissolution and the lowest maintenance of all the tested anodes.

Claims

1. An electrolytic treatment device having

- an anodic compartment comprising a chromium(VI) free etching solution as anolyte and immersed therein an anode,
- a cathodic compartment comprising a cathodic solution comprising an inorganic acid as catholyte and immersed therein a cathode,
- a membrane separating the anodic from the cathodic compartment

characterised in that the anode and/or the cathode comprise a ternary or higher Pb alloy with Sn and at least one further metal selected from the group consisting of Sb, Ag, Co, Bi, and combinations thereof.

2. The device according to claim 1, **characterised in that** the at least one further metal is Sb, Bi or Ag.

3. The device according to any one of claims 1 or 2, **characterised in that** the alloy comprises from 85 to 95 wt.-% of Pb, preferably from 87 to 93 wt.-% Pb, more preferably from 89 to 92wt.-% Pb.

4. The device according to any one of claims 1 to 3, **characterised in that** the alloy comprises from 0,5 to 10 wt.-% of Sn, preferably from 1 to 8 wt.-% Sn, and more preferably from 1,5 to 7 wt.-% Sn.

5. The device according to any one of claims 1 to 4, **characterised in that** the alloy comprises from 0,05 to 10 wt.-% of the third metal, preferably from 0,5 to 8 wt.-% of the third metal, and more preferably from 1 to 7wt.-% of the third metal.

6. The device according to any one of claims 1 to 5, **characterised in that** the etching solution consists of

- 47-74 wt% of at least one inorganic acid,
- 2,2-3,8wt% of at least one periodate salts, preferably sodium metaperiodate,
- 0,01-0,06 wt% of at least one manganese salt,
- 0,01-0,64wt% of at least one iodate salt, preferably sodium iodate, and
- water up to 100%.

7. The device according to claim 6, **characterised in that** the inorganic acid of the anolyte and/or the catholyte is phosphoric acid or sulfuric acid, preferably phosphoric acid.

8. Method for etching plastic parts with the following steps:

- a) providing the electrolytic treatment device of any of the claims 1 to 7,
- b) immersing a plastic part in the etching solution as anolyte in the anodic compartment chamber, and

c) applying a current from 1 to 8 A/dm² for re-oxidising the iodate to periodate in the anodic compartment.

9. The method of claim 8, **characterised in that** the temperature during step c) is from 50 to 80°C, preferably from 60 to 70°C.

10. The method according to any of claims 8 or 9, **characterised in that** the re-oxidation rate to re-oxidize the iodate to metaperiodate is from 0,1 to 1 g/Ah, preferably from 0,2 to 0,8 g/Ah, more preferably from 0,3 to 0,6 g/Ah.

11. The method according to any one of claims 8 to 10, **characterised in that** the dissolution of the anode immersed in the etching solution without any current applied is from 0,1 to 3 g/dm² day, preferably from 0,1 to 2 g/dm² day, more preferably from 0,1 to 1 g/dm² day.

12. The method according to any one of claims 8 to 11, **characterised in that** the dissolution of the anode immersed in the etching solution with a current from 0,8 to 1A/dm² current applied continuously is from 0,05 to 0,8 g/dm² day, preferably from 0,05 to 0,7 g/dm² day, more preferably from 0,05 to 0,6 g/dm² day.

13. Use of an electrolytic treatment device of any of claims 1 to 7 for maintain stable the performances of an etching solution and capacity to oxidise plastic parts.

Fig. 1

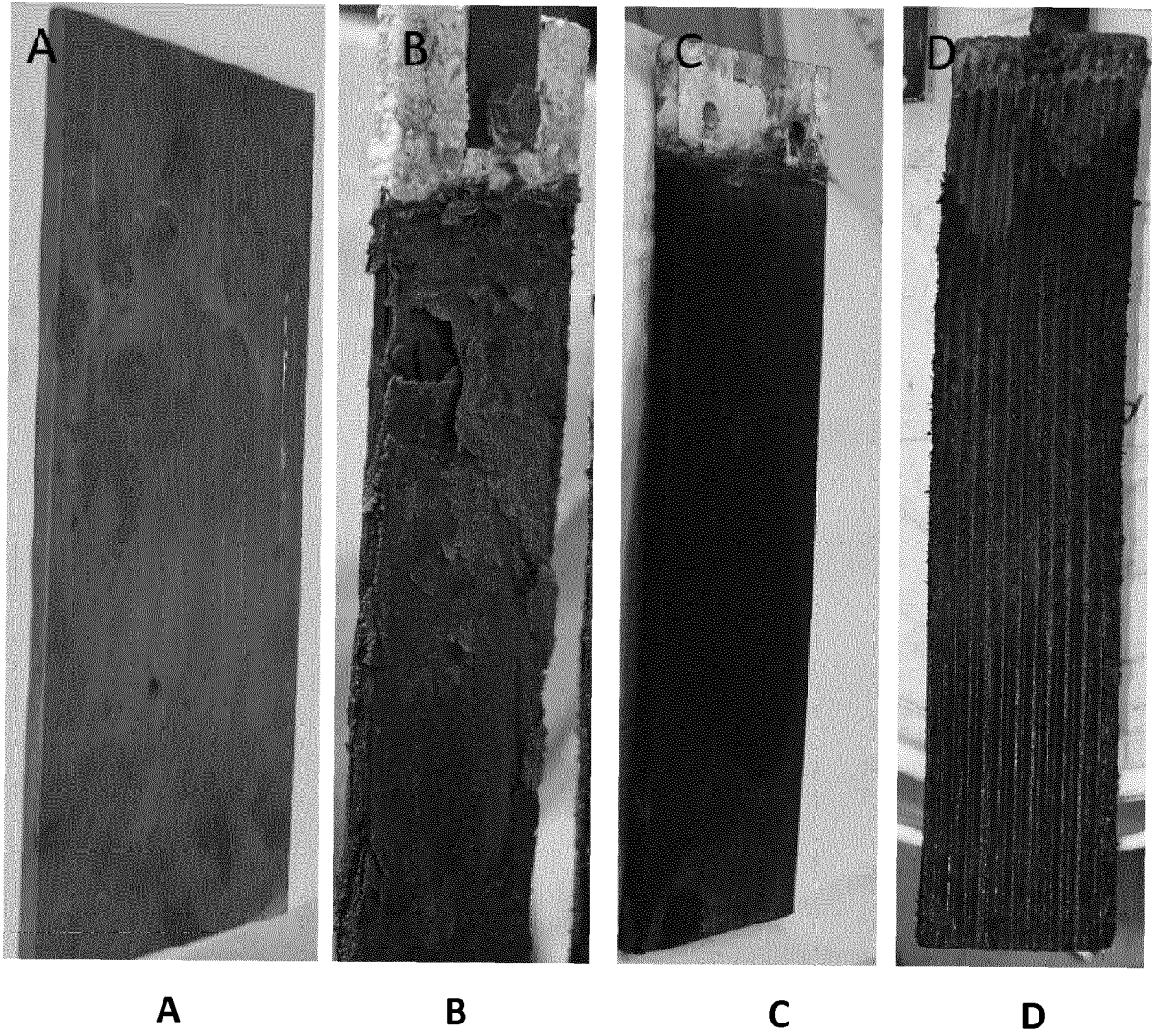
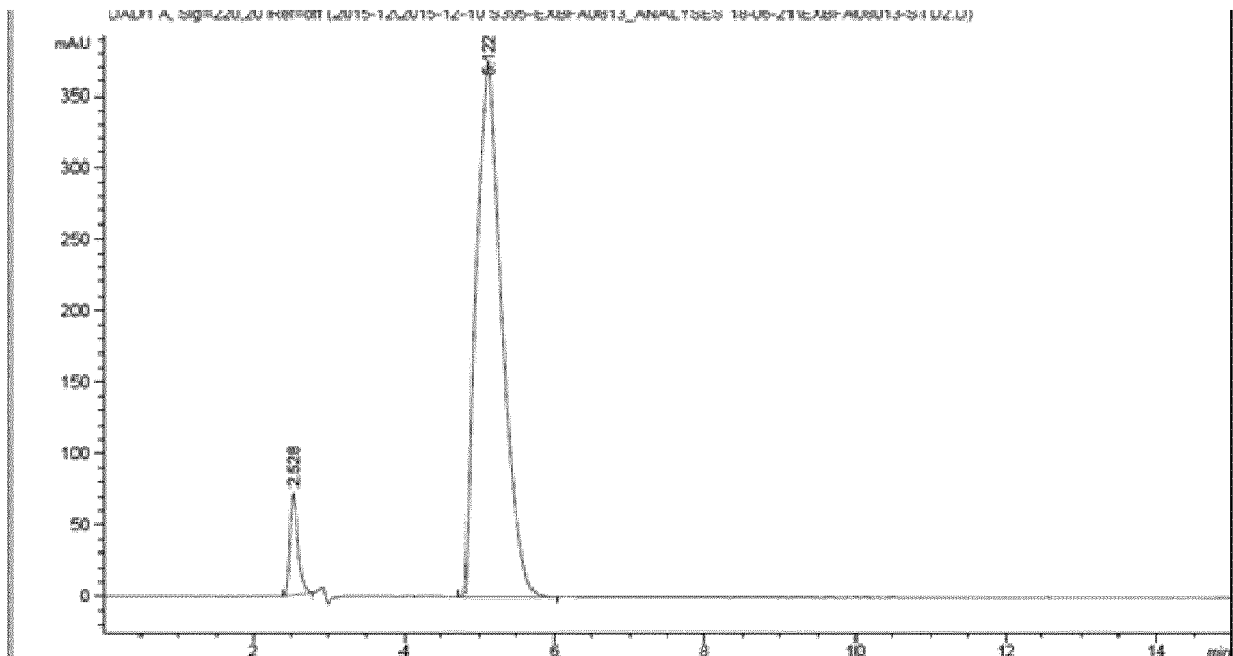


Fig. 2





EUROPEAN SEARCH REPORT

Application Number
EP 19 21 0726

5

10

15

20

25

30

35

40

45

50

55

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2011/089045 A1 (CARDARELLI FRANCOIS [CA]) 21 April 2011 (2011-04-21)	1-5	INV.
A	* paragraphs [0052], [0053], [0090] - [0103] *	6-12	C23C18/24
	* figure 3 *		C25B1/24
	-----		C25B1/28
X	US 4 243 501 A (WRIGHT JR LESLIE S) 6 January 1981 (1981-01-06)	1-5,13	C25B9/08
Y	* column 2, paragraph 15 - column 3, paragraph 34 *	1-5,13	C25B11/04
	-----		C25B11/16
Y	EP 2 971 260 A1 (MACDERMID ACUMEN INC [US]) 20 January 2016 (2016-01-20)	1-5,13	
	* paragraphs [0038] - [0058] *		

			TECHNICAL FIELDS SEARCHED (IPC)
			C23C
			C25B
			C25D
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
The Hague		19 May 2020	Le Hervet, Morgan
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

 1
EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 19 21 0726

5

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

19-05-2020

10

15

20

25

30

35

40

45

50

55

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2011089045 A1	21-04-2011	AU 2009235914 A1	15-10-2009
		BR PI0911653 A2	13-10-2015
		CA 2717887 A1	15-10-2009
		CN 102084034 A	01-06-2011
		EP 2268852 A1	05-01-2011
		ES 2712722 T3	14-05-2019
		JP 5469157 B2	09-04-2014
		JP 2011516730 A	26-05-2011
		SI 2268852 T1	30-09-2019
		US 2011089045 A1	21-04-2011
US 4243501 A	06-01-1981	W0 2009124393 A1	15-10-2009
		ZA 201007214 B	31-08-2011
		AU 517783 B2	27-08-1981
		BR 8001824 A	18-11-1980
		CA 1141701 A	22-02-1983
		DE 3009956 A1	09-10-1980
		DK 137280 A	01-10-1980
		ES 8102599 A1	16-02-1981
		FR 2452303 A1	24-10-1980
		GB 2046793 A	19-11-1980
EP 2971260 A1	20-01-2016	IT 1128101 B	28-05-1986
		MX 153036 A	22-07-1986
		NO 155451 B	22-12-1986
		SE 446198 B	18-08-1986
		US 4243501 A	06-01-1981
		AU 2014249521 A1	27-08-2015
		BR 112015021067 A2	18-07-2017
		CA 2901589 A1	09-10-2014
		CA 2955467 A1	09-10-2014
		CN 105209667 A	30-12-2015
		DK 2971260 T3	23-09-2019
		EP 2971260 A1	20-01-2016
		ES 2745071 T3	27-02-2020
		HR P20191626 T1	13-12-2019
		HU E045344 T2	30-12-2019
		JP 6167222 B2	19-07-2017
		JP 2016512574 A	28-04-2016
		KR 20150126935 A	13-11-2015
		LT 2971260 T	25-09-2019
		PL 2971260 T3	31-03-2020
		PT 2971260 T	27-09-2019
		SI 2971260 T1	31-12-2019
		TW 201500593 A	01-01-2015
		W0 2014164272 A1	09-10-2014

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 5403535 B [0007]
- JP 2006225693 B [0008]

Non-patent literature cited in the description

- **CLANCY, M. ; C. J. BETTLES ; A. STUART ; N. BIRBILIS.** The influence of alloying elements on the electrochemistry of lead anodes for electrowinning of metals: A review. *Hydrometallurgy*, January 2013, 131-132 [0009]